REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE	2. REPORT TYPE Professional Paper	3. DATES COVERED

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Electrochemical Impedance Spectroscopy Evaluation of Primed BMI-Graphite/Aluminum Galvanic System	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Rimi Rivera; Narinder Mehta	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Naval Air Warfare Center Aircraft Division 22347 Cedar Point Road, Unit #6 Patuxent River, Maryland 20670-1161	

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Use of bismaleimide (BMI)-graphite composite materials is on the rise in engineering applications, especially in the design of new state-of-the-art DOD and U.S. Navy aircraft. The primary advantage of BMI-based systems is the increase in service temperature range over conventional epoxies from approximately 300-350 to 400-450 deg F.

During manufacture of aircraft components, as well as repairs to items damages in-service, BMI-graphite and aluminum parts need to be assembled together using either adhesives or fasteners. Under appropriate moisture conditions, a galvanic cell is established within the BMI-graphite/aluminum assembly that could result in degradation of the BMI resin. Real time recognition of this degradation during its early stages is essential in establishing a successful plan to correct the problem. Earlier Navy work performed in 2000 demonstrated that Electrochemical Impedance Spectroscopy (EIS) is a viable analytical technique that can be used for detection of BMI degradation at the molecular level prior to any visual evidence of the failing critical component made of the composite material.

The work presented here provides EIS results on the performance of several configurations of titanium-bolted, primed BMI-graphite/aluminum assemblies exposed to 3.5% salt water at 180 deg F. Epoxy primer, following military specification MIL-P-23377, was applied to all surfaces prior to testing.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Rimi Rivera
a. REPORT	b. ABSTRACT	c. THIS PAGE Unclassified		14	19b. TELEPHONE NUMBER (include area code) (301) 342-8036

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

20010824 078

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY EVALUATION OF PRIMED BMI-GRAPHITE/ALUMINUM GALVANIC SYSTEM

Rimi O. Rivera and Narinder K. Mehta
Naval Air Warfare Center, Aircraft Division, Patuxent River, MD

Use of bismaleimide (BMI)-graphite composite materials is on the rise in engineering applications, especially in the design of new state-of-the-art DOD and U. S. Navy aircraft. The primary advantage of BMI-based systems is the increase in service temperature range over conventional epoxies from approximately 300-350 to 400-450°F.

During manufacture of aircraft components, as well as repairs to items damaged in-service, BMI-graphite and aluminum parts need to be assembled together using either adhesives or fasteners. Under appropriate moisture conditions, a galvanic cell is established within the BMI-graphite/aluminum assembly that could result in degradation of the BMI resin. Real time recognition of this degradation during its early stages is essential in establishing a successful plan to correct the problem. Earlier Navy work performed in 2000 demonstrated that Electrochemical Impedance Spectroscopy (EIS) is a viable analytical technique that can be used for detection of BMI degradation at the molecular level prior to any visual evidence of the failing critical component made of the composite material.

The work presented here provides EIS results on the performance of several configurations of titanium-bolted, primed BMI-graphite/aluminum assemblies exposed to 3.5% salt water at 180° F. Epoxy primer, following military specification MIL-P-23377, was applied to all surfaces prior to testing.

INTRODUCTION

Advances in science and engineering in fiber-reinforced polymer composite materials continue to expand their application as improvements are made to the chemical, thermal and mechanical characteristics of the materials. Their strength and stiffness are comparable to high strength steels and with densities lower than aluminum, these materials have extended their use beyond that of cosmetic to critical structural applications. These applications include lighter, yet stronger materials for aerospace applications, especially in the design of new-state-of-the-art DOD and U. S. Navy systems.

Graphite-reinforced Bismaleimide (BMI)-graphite composite materials are capable of increasing the service temperature from 350° to 450° F of aircraft components as compared to aerospace-grade epoxies. The increased use of this material in aerospace industry requires the inclusion of aqueous environmental conditions in service-life testing. Field operations require the assembly of composite materials to steel or aluminum parts, which result in significant electrochemical polarization (or degradation) of the polymeric resin due to the development of galvanic couple between the noble graphite fibers and active metal[1]. In addition to the corrosion damage to the anodic material, studies have indicated[2] damage to cathodically polarized

graphite-filled composite matrix. The degradation of the polymeric material in saltwater environmental conditions may be realized through damaged graphite fiber edges in the matrix[3], broken reinforcements[4], crazing or cracking of the matrix[5], or debonding at the fiber-matrix or interlaminate surface[6].

The degradation of BMI resin in titanium-bolted, BMI-graphite/aluminum configuration is due to the development of a galvanic couple under aggressive saltwater conditions. It may be either due to reduction of oxygen on the graphite surface to produce hydroxyl ions, which may attack the imide backbone in the matrix, hydrogenation of the imide linkage, or delamination of the fiber/resin interface due to polarization or hydrogen gas generation. Probably, hydrogen gas production delaminates the resin from the graphite fibers, and hydroxyl ions attack the imide matrix system. However, the general notion is[7] that the degradation of BMI resin is due to its lack of resistance to hydroxyl ions produced during cathodic reduction of oxygen in the presence of water at the graphite fiber interface or broken fiber edges[3] as a result of active metal corrosion.

The electrochemical generation of hydroxyl ion may be controlled by surface modification of the BMI-graphite composite or by modifying its polymer character to resist water and hydroxide absorption. The desired approach to inhibit the production of hydroxyl ions is to modify the composite surface/ graphite-resin interface so that the galvanic coupling does not provide the optimum potential of +0.401V required for the reduction of oxygen. Silanization[8] may be an appropriate technique, which may enhance the hydrophobic character of the polymer resulting in reducing its water retention drastically and, thus, control the production of hydroxyl ion.

Treatment of the BMI-graphite composite surface with a primer or a topcoat is another option to inhibit the development of galvanic couple. Primer treatment of high strength structural aluminum metal alloys, such as 7075-T6 and 2024-T3, is a common practice in aerospace industry to avoid damage to these alloys caused by any accidental scratch to the topcoat. This is especially important in Navy aircraft, which perform in highly aggressive ocean environment. Small cracks resulting from exposure to the operating environment may contain a condensed phase of moisture of usually low pH. If accidentally scratched, conventional paint coatings over aluminum alloys may leave the underling metal exposed to the environment. Earlier[9] Electrochemical Impedance Spectroscopy (EIS) work demonstrated that a primer coat can protect a surface from coming in direct contact with the environment, thus inhibiting the onset of degradation mechanism to induce corrosion. The primer is not a barrier coating. It will degrade with time to allow seeping and diffusion of water and electrolytes to help develop active electrochemical sites on the cathodic graphite in the BMI-graphite composite resulting in the chemical degradation of the polymeric BMI resin material.

A need arose to quickly detect the onset of degradation of the polymeric material in real time due to concerns over the potential catastrophic consequences associated with the failure or degradation of a composite material part. Naval Air Warfare Center Aircraft Division (NAWCAD) has initiated an effort to assess the potential use of EIS as a diagnostic tool for composite material degradation in the presence of a galvanic couple environment. Earlier Navy work[3] demonstrated that EIS can be used to detect BMI matrix degradation at the molecular level prior to any visual evidence of the failing critical component made of the composite material. In this work, to inhibit the production of hydroxyl ions, BMI-graphite composite and aluminum base plates for titanium bolted assemblies were primed with MIL-P-23377 epoxy primer prior to assembly. Primer thickness was 2-3 mils (0.002-0.003 inches). Also, in one of the configuration, aluminum plate in the epoxy-primed titanium-bolted BMI-graphite assembly had

2-mil (0.002-inch) groove mark to accelerate the onset of galvanic couple. This paper will summarize the use of EIS to evaluate the performance of titanium-bolted, primed and unprimed BMI-graphite composite/aluminum assemblies exposed to 3.5% sodium chloride (NaCl) electrolyte at 180°F.

MATERIALS AND TEST METHODS
Test Assemblies
The focus of the experiment was to simulate the galvanic couple created in BMI-graphite/aluminum joints under "real world" aircraft environmental exposure conditions. Specimens were prepared using Hexcel Corporation's 5250-4/IM7 BMI-graphite material attached to a 7075-T6 aluminum plate using a titanium (Ti) bolt. Sixteen plies, in a unidirectional configuration, were used to fabricate the BMI-graphite plate. Both sides of BMI-graphite composite (~22.9 cm x ~5.1 cm) and the aluminum (~10.2 cm x 5.4 cm) plates were primed with MIL-P-23377 epoxy primer and allowed to cure at room temperature for two weeks before assembly with a titanium bolt into the test configuration shown in Figure 1. In one of the test configurations, a 2-mil (0.002-inch) groove, shaped like an "X", was milled thru the primer to expose the bare metal on the upper half of the front face of the aluminum plate to accelerate the onset of galvanic couple. Un-primed bolted configurations were also prepared to obtain baseline EIS data at room temperature.

Figure 1. BMI-graphite/aluminum assembly configuration with "X" grooved on aluminum surface above titanium bolt.
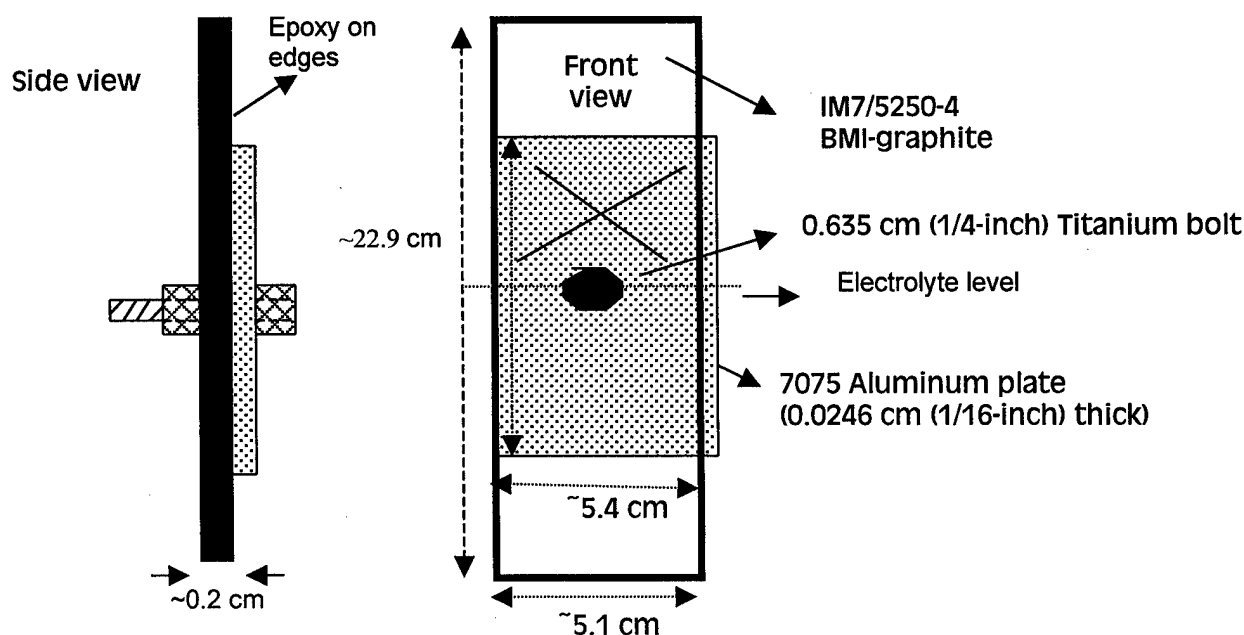
Test specimens were immersed vertically in a rectangular 4-liter Pyrex™ glass chamber containing 3.5% salt-water solution. Testing was conducted in a laboratory oven maintained at 180° F. The top of the chamber had an airtight removable glass plate for the removal and insertion of test assemblies. The water level was maintained at the center of the Ti bolt. In other words, half of the specimen was submerged in the salt-water electrolytic solution while the

other half was exposed to the moisture-saturated air environment. Figure 2 shows a diagram of the exposure setup configuration.

Assemblies were taken out of the solution periodically for evaluation. The EIS test cell was placed on the BMI-graphite surface and the analysis (or test spectra) was performed to establish the electrical characteristics of the specimen. After recording the spectra, the test cell was removed from the BMI-graphite surface, and the assembly was returned to the electrolytic test solution chamber.

Figure 2. Test set up for BMI-graphite/aluminum assembly
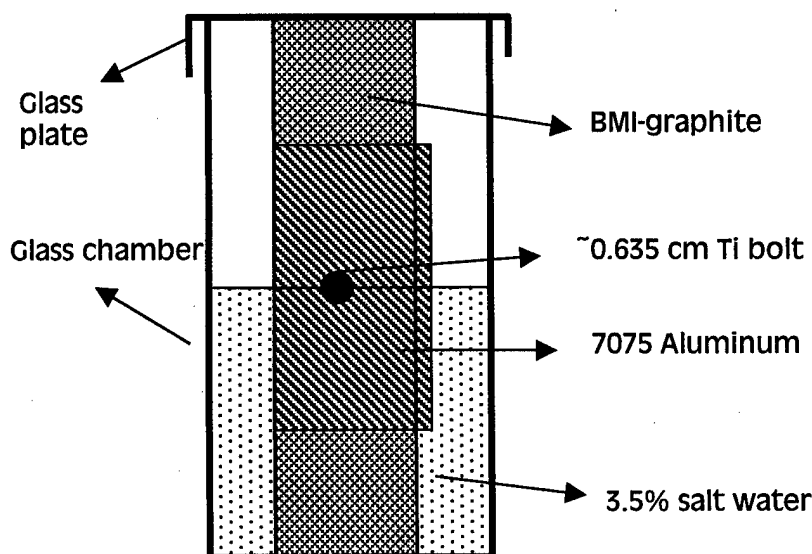

EIS Test Cell

For an optimum EIS test run, specimens were taken out of the salt solution and wiped with paper tissue to remove excess electrolyte solution remaining on the surface. Specimens were maintained in a vertical position to avoid seeping of residual electrolyte embedded between the composite material and the aluminum plate on the section of the specimen immersed in the solution into the portion of the assembly that was not immersed. The EIS test cell consisted of a glass cylinder clamped with an O-ring seal on the composite surface, slightly tilted to avoid seeping of electrolyte. The cell was clamped approximately one centimeter away from the titanium bolt on the composite surface not immersed in the electrolytic solution. The cell area was 7.544 squared centimeters (cm^2). Approximately 30-35 milliliters of 3.5% salt- water solution was added to the test cell for making the impedance measurements. The graphite rod counter electrode and the saturated calomel reference electrode were adjusted to reach about 1 millimeter above the BMI-graphite surface for all the EIS measurements. Figure 3 shows a schematic of the EIS test cell configuration.

Standard instrumental methodology (i.e., Gamry instrument) was used to obtain the frequency dispersion data as a function of exposure time for test specimens immersed in electrolytic solution. A sine wave of +/-10 millivolt amplitude was applied to the cell at the

open-circuit potential, and measured frequencies ranged from 0.1 Hz to 10^5 Hz. AC voltage causes ions to move back and forth between counter and test electrode in response to changing voltage magnitude and polarity. For all test specimens, an equilibrium time of 100 seconds was used for the EIS test runs.

Figure 3. EIS test cell configuration
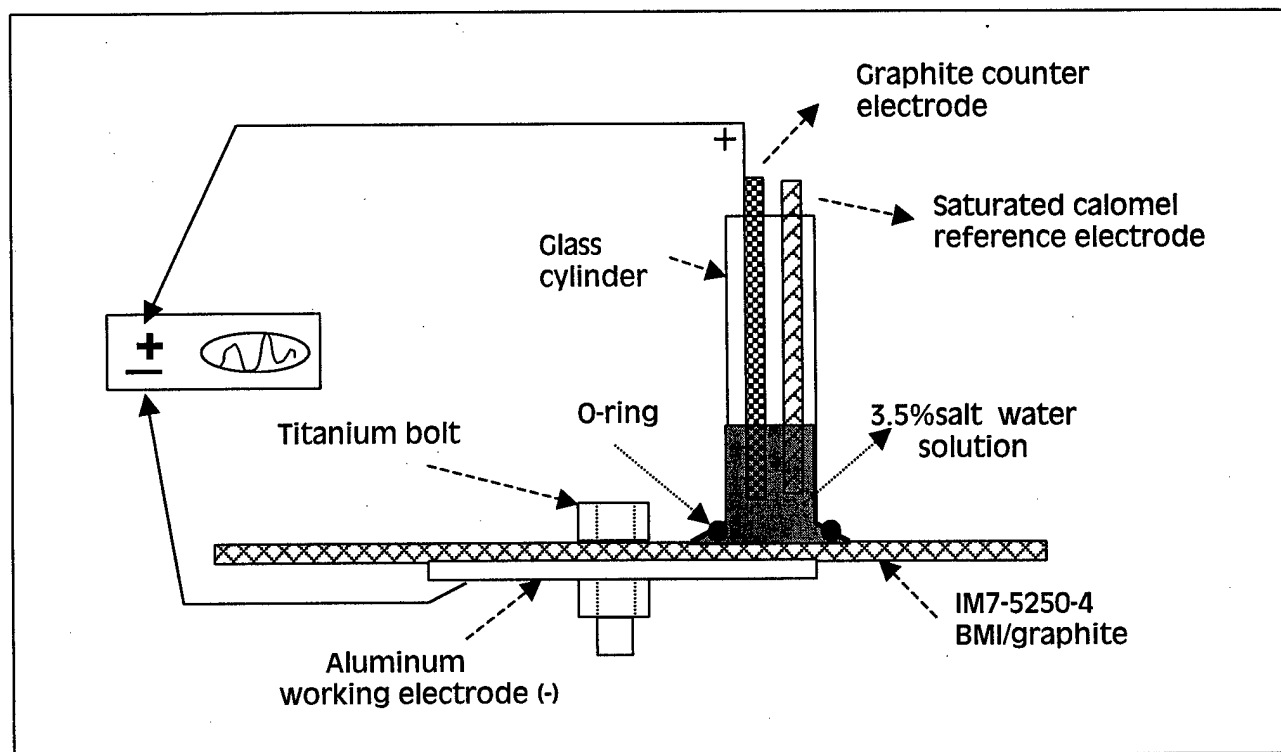
Electrochemical Impedance Spectroscopy (EIS) and Non-linear Least Square Fit (NLLSF) Method

EIS has been widely used as a nondestructive a. c. measurement technique in corrosion detection and monitoring of protective coatings on metal surfaces, and also the mechanisms of protection with time. EIS measurements do not affect the surface irreversibly since it requires only a small amplitude signal (potential) for polarization, and thus can be repeated frequently with time. Details on theory and background on EIS are described elsewhere[3,10]. The logic for using EIS technique to the characterization of electrochemical phenomena developed from the ability to model the electrochemical processes with passive circuit elements (resistors and capacitors). As a first approximation, the electrochemical double layer can be modeled with a capacitor, Faradaic reactions can be modeled with a resistor having a magnitude inversely proportional to the reaction rate, and metal oxides and organic primer or topcoat coatings can be modeled with capacitors.
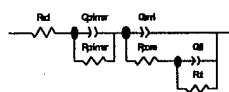
Equivalent circuits using parallel and series arrangements can be used to model complex interfacial processes. The double layer capacitance is sensitive to surface area changes at the atomic level, thus providing information on moisture penetration down the fiber/matrix interface. The kinetics of an electrochemical reaction is nonlinear as suggested by Tafel equation.

Linearity can be maintained by the use of low amplitude excitation (±10mv). One advantage of EIS is that electrochemical processes can be characterized under steady state conditions by superimposing the AC waveform onto a DC potential of interest (open circuit potential) as compared to other electrochemical methods, which must perturb the interface away from equilibrium to acquire needed information. Additional advantage of EIS over measurements in the time domain is that the measured frequency dispersion data can be described analytically employing an equivalent circuit as a model using NLLSF technique. The elements of an equivalent circuit model represent the microscopic processes involved in the transport of mass and charge. The dispersion relations of circuit elements (i.e., resistance, capacitance, Warburg, etc.) may reflect distinct features, which may be related to specific physical processes and to defined sub-circuits of the equivalent circuit model. NLLSF technique adjusts all equivalent model circuit parameters simultaneously, thus obtaining the optimum fit to the measured EIS dispersion data.

Figure 4 shows the series electrical circuit of three time constants used to model the multi-layer structure of epoxy-primed assemblies and the nested equivalent circuit of three time constants used to model the multi-layer structure of unprimed and undamaged specimens. The models were used to evaluate to the frequency dispersion of the experimental data. The models incorporated the solution resistance (R_{ohm}), primer capacitance (Q_{primer}) and resistance (R_{primer}), BMI-graphite composite matrix capacitance (Q_{BMI}), pore resistance (R_{pore}) of the primer and composite matrix due to penetration of electrolyte through defects and pores in the epoxy primer layer as well as in the BMI matrix, (Q_{dl}) is the constant phase element that allows contribution of diffusion at the graphite fiber/moisture interphase region and charge-transfer resistance (R_{ct}) at the fiber/moisture interphase. R_{ct} and Q_{dl} are circuit parameters related to corrosion process and will be interpreted for the system under test evaluation. Interpretation will also be focused on R_{pore} since this parameter is related to the porosity development in epoxy-primer and composite surfaces due to seeping of the electrolyte, water and other ionic species between and through the primer-composite interface.

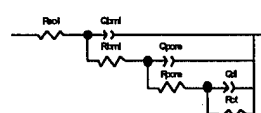Figure 4. Equivalent electrical circuit models used for primed and unprimed assemblies

Series Circuit

Element	Freedom	Value	Error	Error%
Rohm	Free(+)	4.79E-6	NA	NA
Qprimer-T	Free(+)	1.359E-5	NA	NA
Qprimer-P	Free(+)	0.4321	NA	NA
Rprimer	Free(+)	6064	NA	NA
Qbmi-T	Free(+)	4.38E-9	NA	NA
Qbmi-P	Free(+)	0.9949	NA	NA
Rpore	Free(+)	6194	NA	NA
Qdl-T	Free(+)	0.001892	NA	NA
Qdl-P	Free(+)	0.5035	NA	NA
Rct	Free(+)	3280	NA	NA

Data File
Circuit Model File: C:\SA2Models\FF5.md
Mode: Run Fitting/Freq Range(0.1-100000)
Maximum iterations: 100
Optimization iterations: 0
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Nested Parallel Circuit

Element	Freedom	Value	Error	Error%
Rohm	Free(+)	1	NA	NA
Qbmi-T	Free(+)	6.3E-9	NA	NA
Qbmi-P	Fixed(X)	1	NA	NA
Rbmi	Free(+)	0.69	NA	NA
Qpore-T	Free(+)	1E-8	NA	NA
Qpore-P	Free(+)	1	NA	NA
Rpore	Free(+)	1E8	NA	NA
Qdl-T	Free(+)	6E-9	NA	NA
Qdl-P	Free(+)	1	NA	NA
Rct	Free(+)	2E8	NA	NA

Data File
Circuit Model File: C:\SA2Models\PR1.md
Mode: Run Fitting/Freq Range(0.1-100000)
Maximum iterations: 100
Optimization iterations: 0
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

RESULTS AND DISCUSSIONS
Overview

Bode plots were developed for primed and unprimed BMI graphite/aluminum assemblies to illustrate the behavior of both the magnitude of impedance and phase angle as a function of immersion time in 3.5% saltwater electrolytic solution.

Pore resistance, double-layer (diffusion) capacitance, charge transfer resistance and phase angle in the high frequency (i.e., 10^4 Hz) range are major parameters in this evaluation. These parameters may provide sufficient information to understand the mode of inhibiting the chemical degradation of BMI resin in the composite by the primer as well as to the degradation of the polymeric imide backbone in the matrix for un-primed composite samples. Decrease in impedance magnitude and phase angle values with exposure time caused by moisture penetration down the fiber/matrix interface will reflect that the primer barrier coating, as well as the composite matrix integrity, is being compromised.

Phase Angle and AC Impedance

A bode plot for a primed polymeric surface may reveal three distinct[11] responses. The first response is at high frequency (~10K Hz), the second between 1Hz to 10K Hz range and the third at lower frequencies (<1 Hz). Determination of these time responses is important since resistances associated with the low- and mid frequency time constants are related to the corrosion rate. High frequency time constant is not related to the charge transfer resistance in the presence of a primer coating but to some other processes. However, there is evidence[12] that in some cases resistances associated with high frequency portion of the EIS spectrum may probably contain anodic and cathodic contributions to the charge transfer reactions. The middle frequency resistance is normally a pore resistance[11] and reflects that the primed polymeric substrate may probably is exhibiting capacitive dielectric behavior. The resistances associated with low frequency portion of the spectrum probably contain explicit contribution from mass transport both through the fluid and through the porous corrosion products on the surface[12]. Normally, broadening of the low frequency phase angle peak at early exposure time is indicative of the development of corroded areas on the polymeric substrate[13].

EIS Data
Undamaged and unprimed assemblies (F1, F2 and F blk)

The degradation trend of the exposed test assemblies F1 and F2 followed a similar pattern as reported in previous work[3,8] done with similar specimens at room and elevated temperatures. R_{ct} for F1 and F2 decreased drastically within 24 hours of exposure; it was in the range of 10^5 ohms-cm^2 as compared to 10^{10} ohms-cm^2 for the control specimen in air at room temperature (data not shown). The samples degraded completely at a very fast rate within 7-days of exposure time. It was not possible to record EIS spectra for these samples after 7-days of exposure time due to the severity of degradation. Also, Q_{dl} increased drastically within 1-day of exposure reflecting extreme damage to the composite. The data reflected the occurrence of extensive surface adsorption of water/ion species by the polymeric BMI-graphite composite material within 7 days of exposure time. As shown in Figure 5, R_{pore} also decreased drastically within 1-day of exposure time. It reached ~1 ohms-cm^2 for 7-day exposure time as compared to 10^8 ohms-cm^2 for the control sample for the same test period. A drastic decrease in R_{pore} reflects the

development of porosity and absorption of water and other chemical species diffusing along the fiber-matrix interface at a very fast rate to increase the electrochemical sites.

Figure 5. Pore Resistance for un-primed BMI-graphite composite/Al assemblies exposed to 3.5% salt solution at 180°F. No "X" grooved on any surface (undamaged)
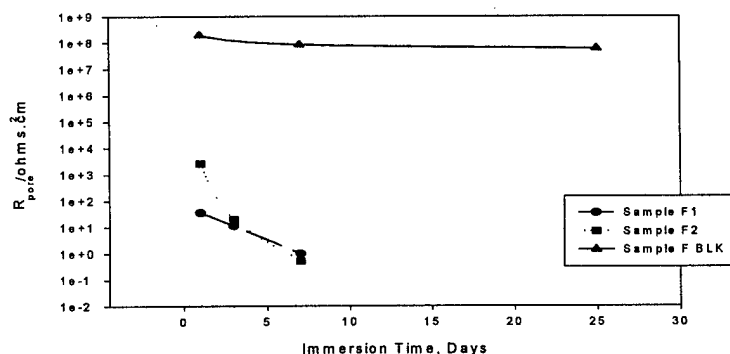
As shown in Figure 6, the shift in Bode phase angle in the high frequency (i.e., 10^4 Hz) range as a function of immersion time was also drastic for the duplicate test assemblies as compared to the control specimen. It reached a value of $< -20^0$ within 1-day of exposure and reached almost zero degree within 7-day of exposure whereas the control sample demonstrated a highly capacitive behavior with $\sim -80^0$ phase angle value in high frequency range. The impedance Bode plots for F1 and F2 assemblies demonstrated a drastic reduction in its slopes within 7-day of immersion time reflecting diffusion and onset of Warburg impedance. The plots also reflect fast kinetics resulting in rapid growth of pores and cavities due to diffusion of electrolyte and other chemical species into the BMI-graphite matrix, and are probably responsible for initiation of side reactions to accelerate the degradation of BMI resin in the composite material. The data has reflected that galvanic couple started developing within hours of exposure of test specimens to 3.5% NaCl at 180^0F. As expected, at the end of the 7-day test period, aluminum plates in the test assemblies were found to be oxidized (or degraded) with white metal hydroxide and chloride gelatin precipitates all around the metal edges and in the solution.

Figure 6. High frequency phase angle for un-primed BMI-graphite composite/Al assemblies exposed to 3.5% salt solution at 180°F. No "X" grooved on any surface (undamaged)
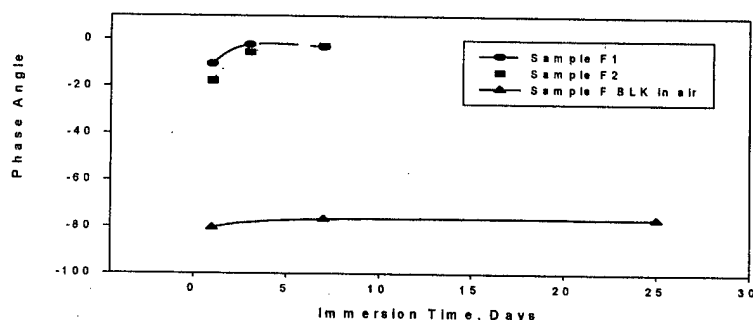
Undamaged and primed assemblies (A1, A2, A3 and A blk)

R_{ct} for A1 specimen was in the range 10^8 - 10^9 ohms-cm^2 for up to 32 days of immersion time and decreased drastically to 4×10^3 ohms-cm^2 between 32-43 days of exposure with a simultaneous increase in Q_{dl} from its approximate value of 10^{-8}-10^{-9} Farad-cm^{-2} for up to 32 days of immersion time to 5×10^{-4} Farad-cm^{-2} between 32-43 days of exposure (data not shown). It reflected onset of corrosion between the metal and composite interface due to diffusion of electrolyte, water and other species. It also reflected that the primer resistance decreased due to diffusion of electrolyte into the interface between the primer and the composite. This diffusion is responsible for the initiation and development of conductive paths for early formation of cavities and delamination of the primer. As shown in Figure 7, R_{pore} for A1 assembly also decreased drastically for between 32-43 days of exposure time reflecting development of porosity and gradual absorption of water, electrolyte and other chemical spies diffusing along the primer-fiber-matrix interface to increase the electrochemical areas. Once the integrity of the primer is compromised due to delamination or development of cracks/crevices in the primer film, it is probable that crevices/blisters on the BMI-graphite composite at microscopic level started growing due to highly electrochemical diffusion activity created by mass and charge transfer. Pore resistance is due to ion conducting paths (fissures) that develop or start growing. The fissures and crevices may act as anodic sites and may help in the degradation of BMI matrix by developing galvanic couple with graphite in the composite.

Figure 7. Pore Resistance for primed BMI-graphite composite/Al assemblies exposed to 3.5% salt solution. No "X" grooved on any surface (undamaged)
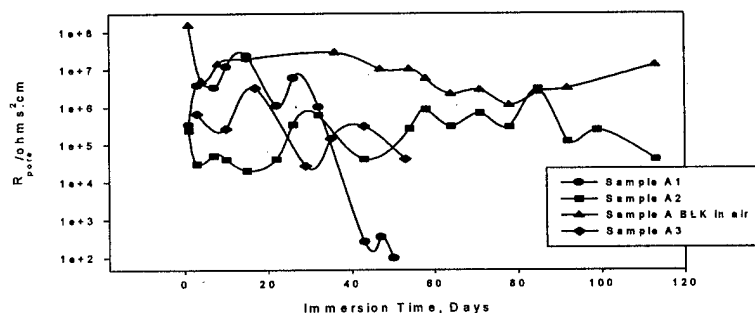
Bode phase angle (Figure 8) in the high frequency range ($\sim 10^4$ Hz) demonstrated a drastic decrease in its value from -86^0 to -10^0 between 32-46 days of exposure time reflecting that pores and cavities started growing due to diffusion of electrochemical species and water into the primer-composite interface, and that it has initiated side reactions to accelerate the degradation of BMI resin in A1 assembly.

Assemblies A2 and A3 demonstrated a constant variation (increase or decrease) in EIS electrochemical parameters reflecting absorption of water at a microscopic level for over 113 and 53 days of exposure time respectively. It reflected that the primer is an excellent barrier to the seeping of the electrolyte under the primer surface, and at the same time inhibiting the development of galvanic couple. It demonstrated that epoxy primer is also an excellent sealant for the broken graphite fibers edges to inhibit the initiation of the reduction of oxygen to produce hydroxyl ions. Results suggest that the primer application to specimen A1 was flawed since it degraded at a much faster rate than replicates A2 and A3. The electrochemical parameters for the control sample in air did not change at all for the test period of over 113 days. A small variation in the values of EIS circuit elements for the control sample reflects the difficulty for the system to detect very low currents through the electrochemical cell.

Figure 8. High frequency phase angle for primed BMI-graphite/Al assemblies exposed to 3.5% salt solution at 180^0F. No "X" grooved on any surface (undamaged)
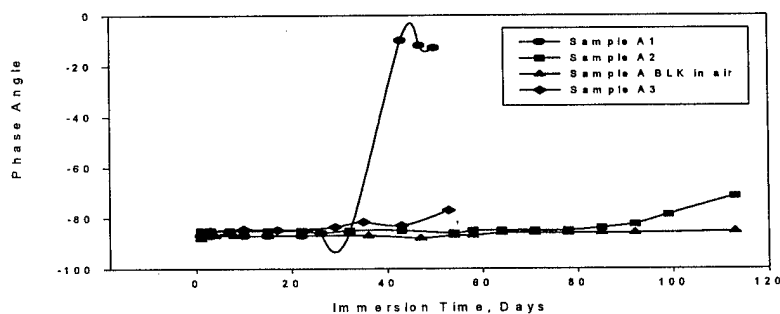
Primed assemblies (B1, B2, B3, B4 and B blk) having "X" grooved on the aluminum surface above the Ti bolt

The purpose of scratching/damaging the aluminum surface by marking a groove "X" was to accelerate the degradation of the primed composite-graphite matrix in a short time as in "real field" environmental conditions. R_{ct} for B1, B2 and B3 specimens were in the range 10^8-10^9 ohms-cm^2 for ~15-32 days of immersion time (data not shown). It decreased after this period with a simultaneous increase in Q_{dl} value from its approximate initial value of 10^{-9} Farad-cm^{-2} to 10^{-4} Farad-cm^{-2} for the same immersion time. It reflected that the primer film degraded quickly and permitted the diffusion of electrolyte and other species to develop conductive paths for the formation of cavities and fissures on the BMI-graphite composite surface. As shown in Figure 9, R_{pore} followed a similar pattern as of R_{ct} reflecting gradual absorption of water along the primer-fiber-matrix interface to accelerate the development of electrochemical sites for the onset of galvanic couple.

Figure 9. Pore resistance for primed BMI-graphite composite/Al assemblies exposed to 3.5% salt solution at 180°F. "X" grooved on Al surface above Ti Bolt.
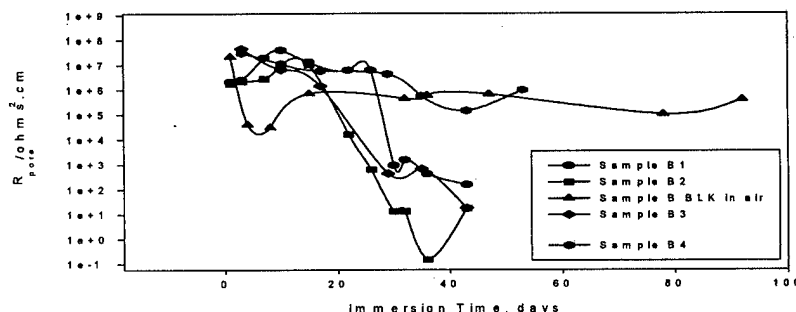

Figure 10 demonstrates the shift in the Bode phase angle in high frequency range for the specimens exposed to the salt solution at elevated temperature. As the surface porosity is increased due to the development of the electrochemical sites such as pores, crevices and fissures, the phase angle in the high frequency range starts decreasing due to gradual deterioration of primer and the composite matrix. Once, the pores and cavities starts growing, it augments the reduction of oxygen in the presence of exposed graphite fibers to produce hydroxyl ions, and thus initiates the BMI-matrix degradation kinetics. It is good to mention that for a pure capacitive impedance (primer/composite not damaged), the phase angle should be ~-90^0. However, if diffusion of electrolyte, water and other ionic species is taking place the phase angle will decrease reflecting porous coating/material and poor adhesion (Warburg impedance). The fact that phase angle and its magnitude are decreasing gradually reflects moisture penetration down the fiber/matrix interface. A close visual look at the exposed B1, B2 and B3 assemblies reflected primer flakes delaminating from the composite surface and the degradation of the BMI resin was visible with the naked eye as shown in Photograph C. Assembly B4 did not demonstrate any onset of degradation for up to 53 days of exposure time. It reflects that the

primer is providing excellent inhibiting effect to electrical induction as well as to the development of microscopic cavities/pores on the primer-composite surface to enhance the onset of galvanic couple and also to the diffusion of electrolyte under the primer-composite-metal interphases.

Figure 10. High frequency phase angle for primed BMI-graphite/Al assemblies exposed to 3.5% salt solution at 180°F. "X" grooved on Al surface above Ti bolt.
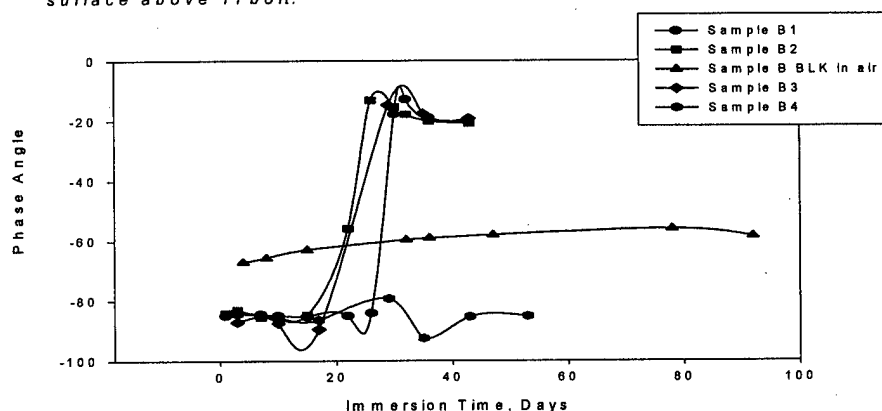
EIS data demonstrated a rather unique trend (decreased magnitude) for control assembly B blk. The values were generally lower as compared to other control assemblies exposed to 3.5% salt solution at room temperature. It may probably be due to induction where, the magnetic field from a. c. electrical current produces a voltage that resists making changes in current magnitude; it is like friction resisting motion. It may also be due to adsorption or desorption equilibrium of surface-active species from the primer (thin or non-uniform coating). It has been suggested that sometimes, individual steps in a complex reaction are slower than others. The slowest step may restrict the EDL (electric double layer) chemical composition changes in response to polarizing voltage magnitude and polarity changes. Restricting EDL chemistry changes can produce induction affecting electrochemical parameters. For these types of specimens, one follows the change in the pattern as a function of exposure time. Electrochemical parameters calculated using the model circuit for the control specimen (B blk) did not change significantly for over 92 days of exposure to the saltwater solution at room temperature.

The general notion that damage to the metal surface (inscribing a groove "X" on its surface) in B assemblies may have played a role in early degradation of the primed BMI-graphite composite specimen exposed to the harsh saltwater environment. For the electrochemical production of hydroxyl ions, exposed graphite edges or surface must be present for an electrical conduction with the metal to initiate the reduction of oxygen to produce hydroxyl ions. In our case, the samples were primed which slowed down the kinetics of hydrogen gas production and hydroxyl ions formation reactions. Application of a primer film has protected the composite resin matrix and has extended its useful life (performance). It has retarded the onset of its degradation mechanism. It is probable that quick oxidation of the exposed scratched metal

anode surface in failed assemblies provided enough driving force (i.e., high electron density and activity) to enhance the onset of galvanic couple with any microscopic localized cavity or pore which may have developed on the graphite surface near the titanium bolt due to a fissure or crack on the primer film. Hence, it is worth to rework quickly any damaged metal surface with a primer to avoid the development of galvanic couple in case damaged graphite sites are exposed at a microscopic level.

CONCLUSIONS

EIS is a viable, non-destructive and quality assurance technique to inspect BMI-graphite structures for damage and degradation of the organic resin resulting from the onset of a galvanic couple. It is feasible to use EIS method to detect BMI-graphite composite degradation at the molecular level prior to any visual evidence of material degradation as well as its detection by other physical instrumental techniques.

The data have demonstrated that epoxy primer is an excellent surface modifier to delay the development of a galvanic couple. It inhibits and slows down the production of hydroxyl ions to attack and degrade the BMI resin in the composite. It has also demonstrated that modification of the BMI surface with a primer can extend the useful life of the BMI-graphite/aluminum structures several folds in "real world" saltwater environments.

ACKNOWLEDGEMENTS

REFERENCES

1. F. D. Wall, S. R. Taylor, and G. L. Cahen, Jr., in: ASTM STP 1174 on High Temperature and Environmental Effects on Polymeric Composites, C. E. Harris and T. S. Gates (Eds.), pp 81-95, ASTM, Philadelphia, 1993.
2. M. A. Dornheim, Aviation Week and Space Technology, 133, 122, Nov. 90.
3. R. O. Rivera, and N. K. Mehta, Evaluation of Bismaleimide-graphite/Aluminum Galvanic System using Electrochemical Impedance Spectroscopy, Report # NAWCADPAX/TR-2000/131, Naval Air Warfare Center, Aircraft Division, Patuxent River, MD, Oct. 2000.
4. D. Hull, An Introduction to Composite Materials, Cambridge University Press, New York, p3, 1981.
5. J. E. Shoutens and K. Tempo, Introduction to Metal Matrix Composite Materials, MMCIAC Tutorial Series, June 1982.
6. W. W. Stinchcomb, and K. A. Reifsnider, Fatigue Mechanisms in Composite Materials- A Review, Virginia Polytechnic and State University, Blacksburg, Virginia, 1979.
7. S. R. Taylor, F. D. Wall, and G. L. Cahen, Jr., The Detection and Analysis of Electrochemical Damage in Bismaleimide/Graphite Fiber Composites, J. Electrochem. Soc., Vol. 143 #2, pp 449-458, Feb. 1996.

8. N. K. Mehta, Electrochemical Impedance Spectroscopic Characterization of Polymer-graphite Composite/ Aluminum Galvanic Systems, Naval Air Warfare Center, Aircraft Division, Patuxent River, MD, Summer 2000 Report.

9. N. Mehta and V. Agarwala, EIS-A tool for coating evaluation of aerospace 7075 T6 aluminum alloys, 1998 U.S. Navy and Industry Corrosion Technology Information Exchange, Louisville, KY, June 17-19, 98.

10. Electrochemical Impedance System Manual and References therein, Gamry Instruments, Inc., Willow Grove, PA, Revision 3.01, May 1998.

11. W. Tait, K. Handrich, S. Tait, and J. Martin, Analyzing and Interpreting Electrochemical Impedance Spectroscopy Data from Internally Coated Steel Aerosol Containers, Electrochemical Impedance: Analysis and Interpretation, ASTM STP 1188, Philadelphia, pp 428-437, 1993.

12. D. Silverman, Corrosion prediction from Circuit Models Applications to Evaluation of Corrosion Inhibitors, electrochemical Impedance: Analysis and Interpretation, ASTM STP 1188, Philadelphia, pp 192-204, 1993.

13. J. Scually, Electrochemical Impedance of Organic-Coated Steel: Correlation of Impedance Parameters with Long-term Coating Deterioration, J. Electrochem. Soc., Vol 136 #4, April 89.